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Fluorinated Single Wall Nanotube/Polyethylene Composites for Multifunctional Radiation Protection

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ABSTRACT

Fluorinated Single Wall Nanotubes (f-SWNTs) have been processed in polyethylene by an incipient wetting technique to achieve a well dispersed nanocomposite for radiation protection. In some cases, samples were further processed using the rapid prototyping method of extrusion freeform fabrication. Composites were exposed to 40 MeV proton radiation with a flux of about $1.7x10^7$ protons/cm^2/sec to a total fluence of $3x10^{10}$ protons/cm^2 .This exposure is consistent with a long-term space mission in low earth orbit. The samples were evaluated by means of Raman spectroscopy and thermogravimetric analysis (TGA). These results were compared to the unexposed composite and unfilled polymer samples. This study has focused on the stability of the nanotube composites when exposed to radiation and prior to hydrogen exposure. It was shown that the stability of the functional group is not constant with SWNTs produced by different processes and that radiation exposure is capable of defluorinating SWNTs in polyethylene.

INTRODUCTION

Since the discovery of single wall carbon nanotubes (SWNTs) in 1993 [1, 2], research has been conducted to exploit their unique mechanical, electrical, and thermal properties to create multifunctional composite materials [3]. Previous research has shown that SWNTs have the highest measured electrical conductivity of any known fiber [4], a higher thermal conductivity than diamond [5], and the highest stiffness of any known fiber [6]. Due to the provocative geometry and other remarkable properties of carbon nanotubes, they are of interest to the aerospace and radiation communities [7-10]. The possibility of nanotubes serving as a storage medium for hydrogen is of particular interest for future spacecraft, and hydrogen-rich and other low atomic mass materials are believed to minimize radiation exposure in the space environment [11]. It is expected that nanotube polymer composites will be effective radiation protection shielding when prepared to contain hydrogen.

Fluorinated and purified SWNTs were used in this work to prepare polyethylene composites. Fluorination is seen as a near term approach for achieving un-roped nanotubes for composite applications, and it may even shorten the tube lengths. As an extension of the work presented in this paper, a sample of f-SWNT/polyethylene composite material was processed and further prepared by extrusion freeform fabrication [12] and submitted to the Materials International

Space Station Experiment (MISSE). Panels containing candidate materials for use in space are installed on the International Space Station (ISS) and exposed to space radiation for approximately three years. The first set of materials, containing the single wall carbon nanocomposites, will be on board the ISS in March 2003 for an eighteen month evaluation. The results of this study will provide a deeper insight into the capabilities of such materials in future space applications.

However, long term space based experiments, are not a practical way of accessing the radiation characteristics of materials, and studies using ground-based energetic particles relevant to the space environment have been limited [13]. In this experiment, SWNT composites were irradiated with 40 MeV protons at Texas A&M University Cyclotron Institute (TAMCI). The proton energies and the total particle fluence used in our work are consistent with the radiation environment of low earth orbit (LEO); such as the environment encountered by the astronauts and electronics of the ISS. To characterize the effects of proton irradiation on nanotubes, the samples were characterized by thermogravimetric analysis (TGA) and Raman spectroscopy. This paper describes some initial results of an ongoing study on the radiation properties of carbon nanotube reinforced materials.

EXPERIMENTAL DETAILS

The SWNTs used in this research were purchased from Tubes@Rice and Carbon Nanotechnologies, Inc. in purified form. These nanotubes were produced by the pulsed laser vaporization [14] and High Pressure Carbon Monoxide (HiPCO) [15] processes respectively. The nanotubes were used in purified (P-SWNT) and fluorinated (f-SWNT) conditions. The fluorination was performed by previously described methods [16]. Medium density polyethylene (MDPE) was obtained from Aldrich in powder form to create the composites. The MDPE had a molecular weight of 6000 and a melting point between 109-111°C. The composite compositions studied are found in Table 1.

The composites were processed by incipient wetting followed by Banbury mixing. The incipient wetting technique creates an initial level of dispersion by coating the polymer with nanotubes [3, 17]. A polymer powder and a nanotube solution were combined and heated in an oil bath to remove the solvent. The remaining material is dried in a furnace to remove the remaining solvent. The over coated polymer is subsequently processed by Banbury mixing and pressed into sheets by heated compression molding. The unfilled polymer was processed in the same manner for consistency.

Each composite sample was placed between two sheets of thin Mylar to facilitate positioning in the proton beam. The samples were irradiated with 40 MeV protons at a flux rate of about 1.7×10^7 p/cm^2/sec to a total fluence of 3×10^{10} p/cm^2 (except in one case). The fluence was chosen to be consistent with the expected exposure during a long-term LEO mission. The irradiations were performed at room temperature in a vacuum of about 5×10^{-5} Torr. The irradiation conditions for the samples are summarized in Table 1.

The samples were characterized by Raman spectroscopy pre- and post-irradiation. The Raman spectroscopy measurements utilized a Renishaw Micro Raman spectrometer with 780.6 nm diode laser and a resolution of 2 cm^{-1} was used. The objective used was 50X with a 0.55 μm aperture. In addition, pieces of each sample were used to perform thermogravimetric analysis (TGA). Both pre-and post-irradiation samples were studied. TGA was performed in a nitrogen atmosphere to ascertain any damage to the polymer caused by the radiation exposure. The

apparatus used was a SDT 2960 from TA Instruments. Weight loss and temperature difference values were used to evaluate the materials.

Table I. Samples studied and radiation conditions.

Sample	Fluence
1.5% wt. SWNT/ MDPE (purified HiPCO)	$3x10^{10}$ protons/cm^2
5% wt. SWNT/MDPE (purified HiPCO)	$3x10^{10}$ protons/cm^2
1.5% wt. f-SWNT/MDPE (laser Tubes@Rice)	$3x10^{10}$ protons/cm^2
5% wt. f-SWNT/MDPE (HiPCO)	$3x10^{10}$ protons/cm^2
1.5% wt. f-SWNT/MDPE (HiPCO)	$4.7x10^{10}$ protons/cm^2
MDPE	$3x10^{10}$ protons/cm^2

RESULTS AND DISCUSSION

Raman spectroscopy results shown in Figures 1-3 of the composites suggest that the proton radiation had a different effect on the samples containing laser generated f-SWNTs compared with the samples containing the HiPCO f-SWNTs. The pre-irradiation spectra of both laser and HiPCO f-SWNT composites were similar as can be seen by the marked peaks of the breathing mode and G band in both curves. The significant features of the pre-irradiation Raman spectra, specifically the broad breathing mode (254.5cm^{-1}) and broad G band (1595cm^{-1}) in Figure 1 of the laser f-SWNTs (Tubes@Rice) composite are still observed in the post-irradiation spectra with no significant change.

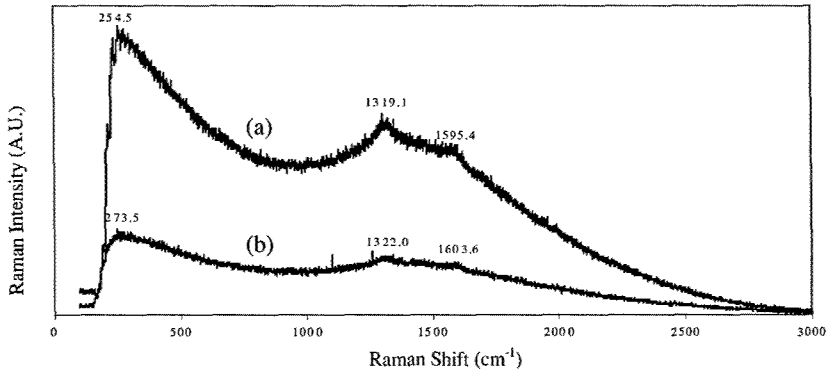

Figure 1. Raman spectra of (a) pre- and (b) post-irradiation of 1.5% wt. fluorinated-SWNT/MDPE (Tubes@Rice, laser).

However, the HiPCO f-SWNT composites appear to defluorinate after radiation. This is observed by comparing the spectra of the irradiated HiPCO f-SWNT composites (Figure 2) with the spectra of both pre- and post-irradiated non-fluorinated HiPCO SWNT composites (Figure 3). The broad features of the pre-irradiated fluorinated composites change to the familiar sharp

and strong lines (around 1590-1600 cm^{-1}) post-irradiation. The non-fluorinated SWNT composites showed no remarkable change in the relevant peaks pre- and post- irradiation as seen in Figure 3. The spectra in Figures 2 and 3 show that percent weight of the SWNTs in the composites played no role in the materials' response to the radiation. The spectra of a control sample of unfilled PE showed no significant change after irradiation.

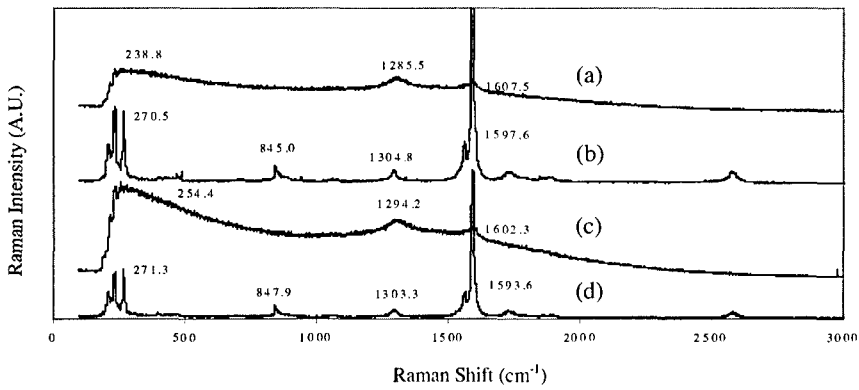

Figure 2. Raman spectra of (a) pre- and (b)post-irradiation of 5% wt. and (c) pre- and (d)post-irradiation of 1.5% fluorinated- SWNT/MDPE (HiPCO).

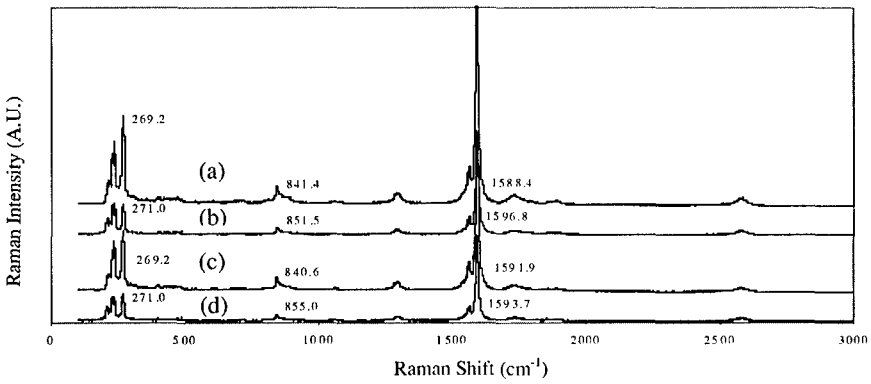

Figure 3. Raman spectra of (a)Pre- and (b)post-irradiation of 1.5% and (c)pre- and (d)post-irradiation of 5% wt. non-fluorinated SWNT/MDPE (HiPCO).

The TGA results in Figure 4, show that no detrimental changes in the thermal degradation properties of the unfilled polymer or the composites occurred due to radiation exposure. All

samples decomposed in one step with the maximum weight loss occurring at a temperature between 469°C and 479°C. The composite containing P-SWNTs and Tubes@Rice f-SWNTs did not show any appreciable change in the temperature where this peak occurred, but the peak position for the composites containing fluorinated HiPCO SWNTs shifted to a higher temperature. In both the 1.5 wt.% and 5 wt.% f-SWNT composites, the inflection point shifted approximately 4°C to correspond with their P-SWNT counterparts corroborating the defluorination observed in the Raman spectra. Figure 4 shows the % weight loss curves and the derivative % weight loss curves in the inset plotted against temperature for the composites containing 5 wt. % P-SWNTs and 5 wt. % f-SWNTs. The curves for the other materials; unfilled polyethylene, 1.5 wt. % f-SWNT (Tubes@Rice)/MDPE, 1.5 wt. % P-SWNT/MDPE, and 5 wt. % P-SWNT/MDPE; agreed within one degree, indicating no radiation-induced damage was observed in these materials.

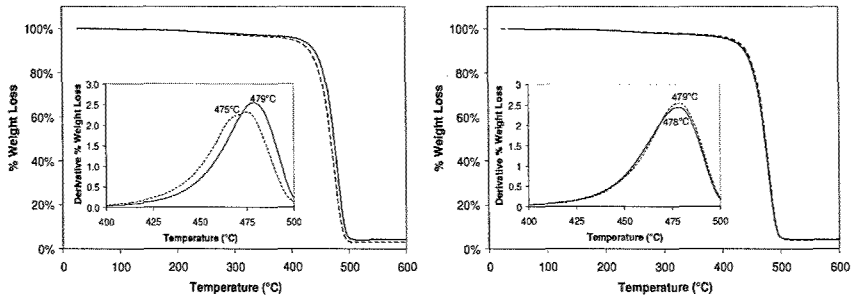

Figure 4. TGA results for the composites containing 5 wt. % f-SWNTs (dashed lines) and 5 wt. % P-SWNTs (solid lines). The left graph shows the TGA data for the composite materials prior to radiation exposure and the right graph shows the TGA data for the materials following radiation exposure. The curves for the composite containing f-SWNTs shift to higher temperatures following radiation exposure suggesting that the fluorine functional groups are removed by the radiation.

CONCLUSIONS

These initial results indicate that radiation exposure with 40MeV protons induces defluorination of the HiPCO SWNTs, as evidenced in the Raman spectra and by TGA results. The proton exposures were consistent with a long-term mission in LEO. This is significant since it would serve as a basis to explore future applications of SWNTs in space. A similar effect is not observed in the Tubes@Rice fluorinated SWNTs processed by the pulsed laser vaporization. Further experiments are planned to study the mechanism behind the defluorination. These results may provide the basis for exploring beneficial attributes of radiation on multifunctional nanotube materials.

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